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Preliminary Studies on the Use of Acid-Soluble Cellulose Acetate Internal Capsules for Workplace Metals Sampling and Analysis

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OVERVIEW

Particles entering filter cassettes used to collect samples of aerosol can deposit elsewhere than on the filter. One suggested procedure for ensuring that those deposits are included in the analysis is to collect them within an internal capsule that can subsequently be digested along with the filter. An inter-laboratory evaluation was carried out to evaluate the use of cellulosic capsule inserts for their suitability in the determination of trace elements in workplace air samples. The inter-laboratory study (ILS) was performed in accordance with an applicable ASTM International standard practice, ASTM E691, which describes statistical procedures for investigating inter-laboratory precision. Performance evaluation materials consisted of prototype cellulose acetate capsules attached to mixed-cellulose ester filters, which were spiked with lead-containing materials (aqueous salt solutions, certified reference soil and paint) at ≈ 20 and ≈ 50 μg Pb per sample. Triplicates of each spiked capsule plus media blanks were conveyed to each volunteer laboratory; spiking levels were unknown to the participants. The laboratories were asked to prepare the samples by acid digestion and analyze aliquots of extracted samples by atomic spectrometry procedures described in applicable ASTM International standard test methods D7035 and/or D7439. Participants were then asked to report their data in units of μg per sample. Preliminary inter-laboratory precision and recovery estimates from six participating laboratories demonstrated the utility of the cellulosic capsule inserts for the measurement of sampled trace elements.

INTRODUCTION

To perform workplace air monitoring in the United States and many other countries, personal samples of airborne particles have historically been collected by pulling air (via suction) through a filter housed in a holder known as a sampler or cassette, and subsequently

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analyzing the filter deposit.⁽¹⁾ However, analysis of only the filter deposit falls short in its ability to properly quantify worker exposures to airborne metals in that it underestimates the airborne exposure, thus potentially giving a false assurance of compliance and protection.⁽²⁾ This underestimation results from a significant accumulation of sampled particles on internal sampler walls that is not included in many analytical procedures.^(2,3) A significant mass of material, up to or even exceeding that found on the filter, can be deposited on the internal surfaces of the air sampling device during sampling and subsequent handling.^(2–8) Sampling for airborne metal dusts in occupational environments requires the evaluation of all particles entering the sampler, whether or not they are found on the filter.^(2–5) Procedures to incorporate this material, such as wiping⁽⁴⁾ or rinsing,⁽⁹⁾ with the filter for subsequent analysis, are labor intensive.

An internal capsule attached to the filter that would contain all collected particles (and could be digested easily without compromising the analysis through background or interference) would be preferable to the use of labor-intensive procedures. Reported here are the results of an investigation using prototype cellulose acetate capsules attached to mixed cellulose ester (MCE) filters. These capsules are similar to those polyvinyl chloride (PVC) capsules currently commercially available and used for gravimetric analysis of collected particulate matter.⁽¹⁰⁾ Following sample collection, the cellulosic internal capsules can be subjected to acid dissolution and subsequent analysis, thereby obviating the need for rinsing or wiping of internal cassette surfaces.

We intend to evaluate and validate a method that accounts for all aerosol particles that enter the sampler, thereby including material that is not otherwise measured by filter-only analysis procedures. The aim of this work was to carry out an inter-laboratory study (ILS) to evaluate the analytical suitability of cellulosic capsule inserts for use with traditional plastic air sampling cassettes. The ILS analysis involved dosing the filter capsule inserts with metal-containing reference materials and submitting them to volunteer laboratories, where the inserts were acid digested and then analyzed for their metal content. It is anticipated that the results from this and subsequent studies will be used in methods that are or will be published in the *NIOSH Manual of Analytical Methods* and through consensus standards bodies such as ASTM International and the International Organization for Standardization (ISO).

EXPERIMENTAL

Preliminary Studies

Prototype cellulose acetate internal capsules (“Accu-Caps”) attached to 0.8 micron pore size 37-mm MCE filters were provided by SKC, Inc. (Eighty Four, Pa.). These internal capsules are designed to be inserted into 37-mm plastic cassette samplers as shown in Figure 1.

Background elemental levels in prototype cellulosic Accu-Caps—after hotplate digestion in $\text{HNO}_3/\text{H}_2\text{O}_2$ with subsequent analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES)⁽¹¹⁾ and inductively coupled plasma-mass spectrometry (ICP-MS)⁽¹²⁾—are shown in Table I. These results demonstrated that background levels of metals and metalloids were for the most part insignificant, although for certain elements correction might be required during analysis.

One element of particular importance in this regard is lead (Pb). Samples of cellulose acetate material equivalent to the mass used in preparing Accu-Caps were sent to other laboratories, which returned inconsistent values for lead, up to around $1+1\text{ }\mu\text{g}$ (2 standard deviations, SD). Since this value is relatively large with respect to the amount expected on a filter (e.g., $15\text{ }\mu\text{g}$ for a 4-hr sample at the Occupational Safety and Health Administration (OSHA) Action Limit⁽⁴⁾ of $30\text{ }\mu\text{g}/\text{m}^3$), lead was considered a critical element for the evaluation of cellulosic Accu-Caps.

Inter-Laboratory Analysis

Two inter-laboratory round-robin trials were undertaken in which cellulosic Accu-Caps spiked with lead-containing material were conveyed to participating laboratories. The inter-laboratory trials were carried out according to ASTM E691,⁽¹³⁾ which requires a minimum of six participating laboratories. The first inter-laboratory trial contained samples spiked with solutions of lead acetate, as well as samples doped with 50 mg of powdered reference materials (paints and soils) containing verified loadings of lead prepared by a contract laboratory. The paint and soil reference materials used had been previously prepared to prepare samples for the AIHA[®] Environmental Lead Proficiency Analytical Testing Program.⁽¹⁴⁾

The second round did not include the filters spiked with lead acetate solution—only additional Accu-Caps fortified with 50 mg of verified loadings of lead-containing paint and soil reference materials. Lead loadings in the spiked Accu-Caps reported by the contract laboratory for quality control purposes are shown in Table II. Note that although the standard deviation for the high lead acetate spikes is larger than that for the other samples, it met the control criterion of being within $\pm 5\%$.

Spiked Accu-Caps loaded into 37-mm plastic cassettes (SKC, Inc.) were transported by commercial courier to CDC/NIOSH for further shipment to eight volunteer laboratories. Participants were requested to carry out digestion and analysis of the Accu-Cap inserts using their preferred procedure(s) in accordance with applicable consensus standards.^(11,12) Following analysis, the participants were asked to report their results to the coordinator of the study in units of micrograms of lead per sample.

Seven participants returned results in the first round, but it was obvious from observation and subsequent analytical results that jostling in shipment had caused loss of the spiked dusts from the capsules into the space between the capsule and the cassette. The plugs provided with the cassettes did not reach far enough to also plug the hole in the top of the Accu-Cap. Thus, only the solution-spiked results were evaluated in this round. One laboratory did not provide results at all, and another reported much higher values than the others; these were considered as outliers. For the second round, longer custom plugs had been obtained for closing the top of the cassettes. However, even with these plugs, the severity of jostling in shipment to certain countries was so great that the dust migration problem was not eliminated. Ultimately, six participants (Table III) returned acceptable results for both rounds. For data presentation, laboratories were identified by code to ensure confidentiality.

RESULTS

Summarized ILS results for lead measurements of spiked Accu-Caps, aqueous spikes from the first round, and soil and paint spikes from the second round—treated statistically in accordance with ASTM E691⁽¹³⁾—are presented in Table IV. In this table, s_x is the standard deviation of the mean value as estimated by the average of all ILS results for a given material, and the repeatability standard deviation s_r is the average within-laboratory standard deviation for each reported result. The reproducibility standard deviation s_R (the pooled within-laboratory and inter-laboratory standard deviation) is obtained from

$$s_R = \{(s_x)^2 + [(s_r)^2(n-1)n^{-1}]\}^{1/2} \quad (1)$$

where n is the number of test results at a particular spiking level.⁽¹³⁾ Repeatability ($r = 2.8s_r$) is an approximate 95% confidence limit on the within-laboratory variability, while reproducibility ($R = 2.8s_R$) is an approximate 95% confidence limit on the pooled within- and between-laboratory variability.

Each laboratory was supplied with three blank Accu-Caps in cassettes in the first round and two in the second round. Variable blank levels of lead in the unspiked capsules (up to 2.5 µg Pb) were reported by some laboratories, but the reporting limits of laboratories varied considerably. Many labs had much higher reporting limits, so blank values could not be effectively evaluated, and no blank results are presented. However, blank values when reported were not subtracted from sample values, and thus, any variability contribution from this source is incorporated in the ILS results.

DISCUSSION

The results of Table IV demonstrate quantitative lead recoveries from the spiked Accu-Caps, as mean recovery was within 100% ± 10% for most sample matrices. In the case of the high aqueous lead acetate loading, which had the highest variability in the quality assurance samples analyzed by the contractor, the source of the low recovery and high variability is likely to be the preparation of the samples rather than the analysis. The ILS results also showed excellent intra-laboratory precision—given repeatability between ≈4 and ≈7% for all but the high aqueous spikes—well below typical target maximum repeatability for inter-laboratory analysis of 15–20%.⁽¹⁵⁾ Even the repeatability for the high aqueous spikes (16%) is within the desired range. Results for reproducibility are similar (between ≈4 and ≈10%), although the reproducibility for the high aqueous spikes (16%) is again higher. These data indicate that (1) the use of cellulosic Accu-Cap inserts for sampling and analysis of metals such as lead is a viable and workable methodology for occupational air sampling, and (2) blank results do not appear to contribute to the recovery or the variance. The results are especially encouraging in view of the use of realistic environmental matrices for spiking, and the fact that participating laboratories were free to choose their preferred sample preparation and analysis procedures (within the confines of options given in the standard methods that the labs were asked to follow).

After the problems, due to sample transport during the first ILS round and noted above, changes to the design of the sampler closure were made prior to the second round, which was much more successful. Custom longer plugs that would cover the capsule inlets were requested from the manufacturer. However, it was noticed that the depth to which these plugs entered the top hole of the sampling cassette varied considerably, so that some Accu-Caps were still not being adequately plugged, which resulted in losses of loose material. In addition, some capsules and cassette holes did not line up well enough to allow the plug to penetrate the Accu-Cap, and the plug depressed the dome of the internal capsule. Fifty milligrams is a considerable amount of material that was only loosely placed in the capsule and typical air samples consist of no more than a few milligrams of material more strongly fixed to the substrate by electrostatic forces. However, cakes of sampled aerosols that are easily dislodged from the filter are often observed on air sample filters, so similar losses might still occur with real samples.

We found that some cassettes did not fit tightly together, or that some fitted tightly but with a seal above the edge of the internal capsule. While this did not necessarily lead to losses of material within the cassette, it would likely have led to losses in sampling.⁽¹⁶⁾ Finally, in the development of air samples for the next ILS round, it was noted that about 3% of Accu-Caps had very high pressure drops and were unusable. As has been noted previously, this results from regions with limited porosity within the cellulose ester filter.⁽¹⁷⁾ It is an issue generally for filters and not a problem with the capsules containing the filters.

Proper fitting of parts can be assured at source if the manufacturer produces cellulosic Accu-Caps pre-assembled in cassettes. This is reasonable since the mass of cellulose is too variable to allow weighing. Nevertheless, it is recommended that all assembled Accu-Caps be checked by the laboratory assembling the cassettes or by the user in the field to ensure that: (1) the internal capsule is securely sealed within the cassette (this can be checked by pulling air through a condensation nucleus counter in line with the cassette, as has been proposed for all cassettes),⁽¹⁶⁾ and (2) the plug fits both the entry orifice of the cassette and the insert and properly seals the Accu-Cap. Assembled Accu-Caps that do not meet these checks should be rejected. To ensure the seal is also good after sampling, it is further recommended that the specific plug/cassette combination be retained for reassembly, for example, by placing the plug in a bag labeled to match the cassette while sampling is in progress.

In summary, lead (Pb) performance data from this ILS demonstrate that the use of cellulosic internal capsules attached to MCE filters gives acceptable inter-laboratory precision and recoveries after acid digestion and atomic spectrometric analysis. The results are important in consideration of the widespread use of the closed-face filter cassette for occupational air sampling for metals.

These inserts can therefore be useful for routine industrial hygiene applications and may be employed in lieu of rinsing and wiping techniques that are otherwise necessary to account for internal sampler wall deposits. A further ILS is in progress using the same laboratories to analyze samples produced by pulling air through Accu-Caps in cassettes from a multi-port chamber that contains desolvated nebulized aerosol that, in turn, contains multiple metal salts.

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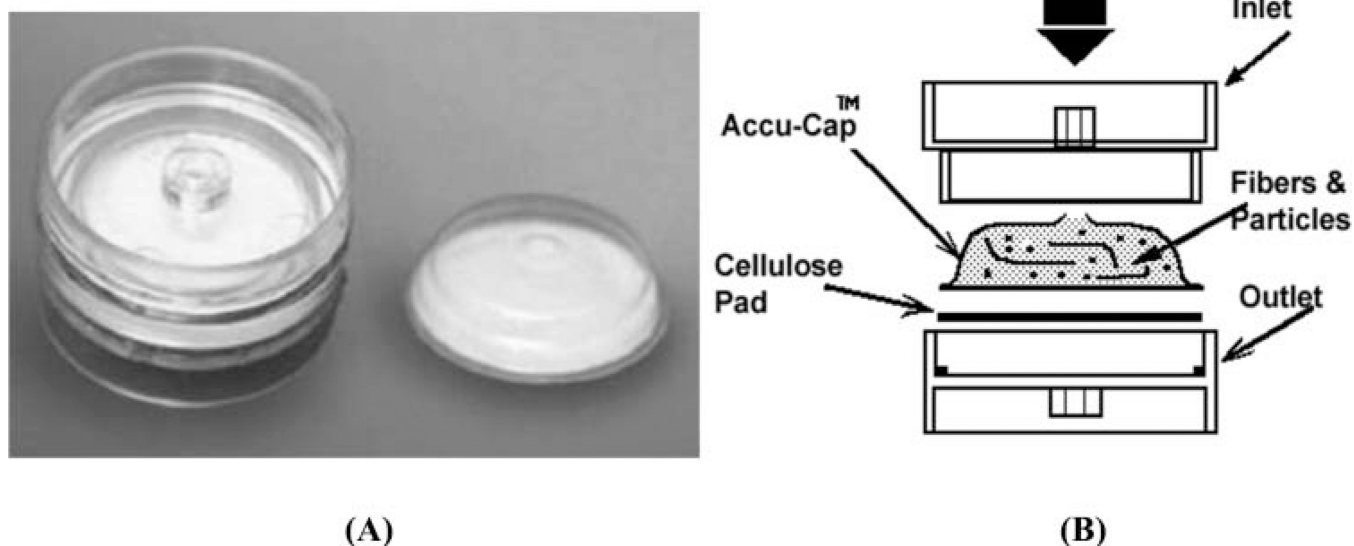


FIGURE 1.
(A) Photograph of 37-mm-diameter plastic sampling cassette (left) and Accu-Cap internal capsule (right). (B) Schematic of cassette sampler showing placement of Accu-Cap insert and cellulose backup pad

Mean Results ($\mu\text{g}/\text{sample}$) from Elemental Analysis of Prototype Cellulosic Accu-Caps Analyzed by NIOSH Contract Laboratory (n = 5)

TABLE I

Element	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Li
ICP-AES	—	ND	ND	0.2	ND	ND	—	0.8	ND	0.2	—	1.0	—
ICP-MS	0.1	0.2	ND	0.1	ND	ND	36	0.1	ND	0.2	1.6	0.8	0.1
Element	Mg	Mn	Mo	Ni	P	K	Se	Sr	Tl	Sn	Ti	V	Zn
ICP-AES	—	ND	ND	ND	—	—	ND	—	ND	—	—	0.2	0.5
ICP-MS	2.2	0.1	ND	ND	6.4	1.3	ND	0.1	ND	0.7	0.2	ND	0.4

Notes: ND, none detected. Detection limits are not reported here for clarity; typical limits of detection are given in the methods.^(11,12)

TABLE II

Lead Loadings of Spiked Cellulosic Accu-Cap Samples Analyzed in Inter-Laboratory Trials

Sample Spikes	Mean Pb (μg) \pm SD
Lead acetate (low)	18.0 \pm 1.5 (n = 4)
Lead acetate (high)	42.1 \pm 3.9 (n = 4)
Soil (low)	22.1 \pm 1.0 (n = 3)
Soil (high)	54.5 \pm 2.1 (n = 3)
Paint (low)	21.3 \pm 0.2 (n = 3)
Paint (high)	51.8 \pm 0.6 (n = 3)

TABLE III

Volunteer Participants in the Cellulosic Accu-Cap Inter-Laboratory Trials

Laboratory	Location
Bureau Veritas North America (BVNA)	Novi, Michigan
Institut de Recherche Robert Sauvé et en Sécurité du Travail (IRSST)	Montréal, Quebec, Canada
Occupational Safety and Health Administration (OSHA)	Sandy, Utah
Savannah River National Laboratory (SRNL)	Savannah River Site, South Carolina
Statens Arbeidsmiljøinstitutt (STAMI)	Oslo, Norway
Wisconsin Occupational Health Laboratory (WOHL)	Madison, Wisconsin

TABLE IV
 ILS Precision Statistics for Lab-Reported Mean Lead Measurements from Spiked Cellulosic Accu-Caps

Sample Matrix	\bar{x} , $\mu\text{g Pb}$	s_x	s_r	s_R	r	R	%Recovery (% RSD)
Lead acetate (low) ^A	18.2	0.99	1.83	1.83	5.13	5.13	101 (5.0)
Lead acetate (high) ^A	37.5	1.92	5.73	5.73	16.1	16.1	89.1 (4.7)
Soil (low)	21.6	2.41	1.62	2.75	4.52	7.70	97.7 (10.2)
Soil (high)	49.8	2.62	2.42	3.28	6.76	9.18	91.3 (4.8)
Paint (low)	22.2	0.46	1.67	1.67	4.67	4.67	104 (1.9)
Paint (high) ^A	49.2	1.31	2.17	2.21	6.08	6.19	95.0 (2.4)

Notes: \bar{x} = overall mean (for $n = 6$ reporting labs); s_x = standard deviation of the laboratory means around the grand mean; s_r = repeatability standard deviation; s_R = reproducibility standard deviation; r = repeatability; R = reproducibility; RSD = relative standard deviation ($s_x \times x^{-1}$).

^A One statistical outlier from a single reporting lab excluded (Q-test, $P = 0.05$).